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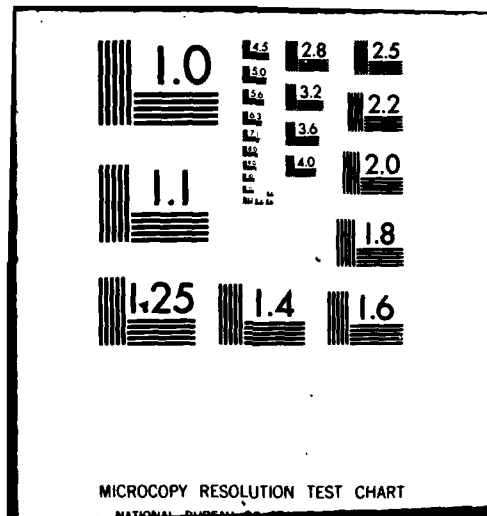
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Final Scientific Report

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Air Force Office of Scientific Research

- Chemistry Branch -

Theory and Experiments on Chemical Dynamics
and Instabilities

by

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- January, 1980 -

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Item 20 (cont) ABSTRACT

propagation of discontinuities in systems with chemical instabilities for the purpose of an analysis of the motion of domain walls in ferrodistorive materials. When a fluid, gas or liquid, is subjected to a temperature gradient in the gravitational field, then convective instabilities, called Rayleigh-Bernard instabilities, may occur. We have re-investigated this much-studied problem since previous work did not consider the inclusion of cross transport coefficients such as thermal diffusion (Soret effect) and the reciprocal phenomena known as the Dufour effect. We used the hydrodynamic equations in the Boussinesq approximation and studied their stability to the onset of both stationary and oscillatory convection. We find a variation principle for the critical Rayleigh number at the onset of stationary convection which depends on a single dimensionless parameter, a function of the thermo-dynamic coefficients. In our study of chemical instabilities, we concentrate on the variety of phenomena which may occur in chemical reaction systems sufficiently far from equilibrium both in homogeneous and inhomogeneous systems. We review stability of stationary states, multiple stationary states, periodic stable oscillations, transitions between stationary and oscillatory states, chemical hysteresis, composed oscillations, the extensive variety of chemical waves, chemiastic instabilities, time-independent spatial structures, and localized chemical instabilities. We have made good progress on assembling and initial testing of a system designed to measure fluctuations far from equilibrium in the chemical reaction $2\text{NO}_2 = \text{N}_2\text{O}_4$ displaced by green laser light. We have started further experimentation on a photo-induced oscillatory chemical reaction, a dilute solution of dimethylantracene in chloroform.

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Final Scientific Report***1. Franck Condon Theory of Chemical Dynamics. Angular Distribution of Reaction Products.**

The Franck Condon approach to the analysis of dynamics is based on a chemist's intuition that electron (bond) rearrangements in a reaction occur at nearly fixed nuclear coordinates. We have used the Franck-Condon theory to calculate planar and three-dimensional angular distributions for the reaction products of atom-diatom chemical reactions. After applying the Franck-Condon approximation we consider the limits of weak and strong potential coupling in the limits of weak and strong kinematic coupling. For assumed LEPS surfaces of the systems $H + H_2$, $H_2 + F$, and $H + Cl_2$, we calculate angular distributions of reaction products in the various coupling limits for ranges of final product states. Angular distributions in the strong potential coupling limit have a Gaussian shape peaked about the backscattering angle. For $H + H_2$ we find our results in the strong potential limit to be in qualitative agreement with exact quantum mechanical calculations. Angular distributions for a given product state broaden as the initial relative kinetic energy is increased in agreement with classical trajectory

*Starred references on the enclosed publication list of the principal investigator have received support from the Air Force Office of Scientific Research.

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calculations ($F + H_2$). The angular distribution is also predicted to broaden as the final relative velocity increases in agreement with experiment ($H + Cl_2$, $F + H_2$).

We next introduce several further simplifying approximations and find that for exothermic reactions like $F + H_2$ the radial contribution to the T matrix is dominated by certain features of the potential: the barrier height, the slope of the potential on the reactant side and force constants in the region of maximum overlap. Our analysis provides a basis for the formulation of reduced variables which may be of use in comparing different reactions. Finally we discuss some sufficient conditions for the separability of product velocity and angular distributions. (142, 149)

2. Dynamics of Domain Walls in Ferrodistorptive Materials.

We have used some results from the theory of propagation of discontinuities in systems with chemical instabilities for the purpose of an analysis of the motion of domain walls in ferrodistorptive materials. Below a critical temperature ordering occurs in such systems and within a given material domains of ordered and disordered material can coexist. On application of external fields the boundaries separating the ordered and disordered domains move. We have constructed a stochastic theory for such systems which improves upon previous work by inclusion of an appropriate dissipative mechanism which assures the asymptotic attainment of a finite velocity of domain wall propagation.

We start from a generalized Langevin equation of motion for the movements of the ions, which includes dissipative terms and external fields, in addition to anharmonic and strain force terms. We obtain large and small amplitude solutions corresponding to domain walls and the usual soft mode phonons, respectively. We show that apart from translation the domain walls are absolutely stable solutions of our equation and that in external fields they reach a unique terminal velocity. The linear dependence of the velocity on the field allows us to define a temperature dependent mobility which is related to the diffusion coefficient for the wall. Furthermore, we calculate analytically the dynamic structure factor, necessary for light scattering, due to domain walls and soft-mode phonons. We find that the Brownian motion of the domain walls leads to a very narrow Rayleigh peak.

We have applied the theory just outlined to the uniaxial displacive ferroelectrics $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and SbSI . We show that the parameters necessary for our theory can be determined from available experimental data for these substances. The values so obtained are physically reasonable. With no adjustable parameters we calculate the wave number, temperature and pressure dependence of the low temperature central light scattering peak for these materials, the density of domain walls and the polarization switching time. The theoretical results agree quantitatively with the experimental data. We predict the as yet

unmeasured temperature-dependent wall diffusion coefficient and the mobility of domain walls in a field.

Ferroelectric materials are important components of many electronic and computer systems.

This work has been written up in two articles and has been published in *Physical Review B*. (144, 145)

3. Hydrodynamic Instabilities.

When a fluid, gas or liquid, is subjected to a temperature gradient in the gravitational field, then convective instabilities, called Rayleigh-Benard instabilities, may occur. We have re-investigated this much-studied problem since previous work did not consider the inclusion of cross transport coefficients such as thermal diffusion (Soret effect) and the reciprocal phenomena known as the Dufour effect. Furthermore, in much of the previous work boundary conditions applied were frequently not physically realistic. We used the hydrodynamic equations in the Boussinesq approximation and studied their stability to the onset of both stationary and oscillatory convection. We find a variation principle for the critical Rayleigh number at the onset of stationary convection which depends on a single dimensionless parameter, a function of the thermodynamic coefficients. For certain ranges of that parameter the system becomes unstable only if heated from below. For a second range the instability may occur only if the fluid is heated from above. For yet a third range there exists the interesting possibility of the onset of instability

if the heating occurs from above or below. We also derive expressions for the amplitude of convective motion and the Nusselt number for both stationary and oscillatory convections. These expressions are then used to show that heat flux measurements may be a useful tool for the study of the onset of instability in binary fluids.

This work has been published. (150, 151, 155, 156)

4. Chemical Instabilities.

We have written two review articles on this subject; one published in *Advances in Chemical Physics*, Vol. 38, and the other accepted for a future volume of *Advances in Chemical Physics*. In the first article we concentrate on the variety of phenomena which may occur in chemical reaction systems sufficiently far from equilibrium both in homogeneous and inhomogeneous systems. We review stability of stationary states, multiple stationary states, periodic stable oscillations, transitions between stationary and oscillatory states, chemical hysteresis, composed oscillations, the extensive variety of chemical waves, chemi-acoustic instabilities, time-independent spatial structures, and localized chemical instabilities. All of the discussion is restricted to a macroscopic treatment. (139)

In the second review article there is some discussion of macroscopic behavior primarily for the purpose of introducing notation. The primary emphasis is on a stochastic analysis including a treatment of fluctuations in systems both near and far from equilibrium. (154)

5. Measurements on Systems with Chemical Instabilities

We have made good progress on assembling and initial testing of a system designed to measure fluctuations far from equilibrium in the chemical reaction $2\text{NO}_2 = \text{N}_2\text{O}_4$ displaced by green laser light. The system consists of the cell containing NO_2 - N_2O_4 , the laser and associated optics, a vidicon optical multiple channel analyzer, and an on-line computation system. Due to a small but more than adequate natural fluorescence of NO_2 we can measure the NO_2 concentration as a function of time and space (at least in a two-dimensional projection). The measurement then consists of recording the concentration of NO_2 in the cell at approximately 10 to 100,000 locations, each 30 milliseconds. This large amount of data is transferred to a tape and is processed from there by the calculation of spatial and temporal autocorrelation functions. All the components of the system have been assembled and most of them have been tested.

We have started further experimentation on a photo-induced oscillatory chemical reaction, a dilute solution of dimethylantracene in chloroform. The oscillations involve both photochemical reactions and diffusion in and out of the imposed light beam at 260 nm. Oscillatory behavior is observed in the fluorescence of dimethylantracene emitted in the range of 400 to 460 nm. We are setting up a series of experiments on this system both in a spectrofluorimeter and in the vidicon collection system.

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